SCIENTIFIC METHODOLOGY ASSESSMENT

COMMITTEE REPORT

by

Steve E. Hrudey
Byron G. Kratochvil
Robert R. Orford
John W. Markham
Ridley K. Shaw

for

Minister of the Environment

Government of Alberta

July 1983

EXECUTIVE SUMMARY

Studies by Sciex and the Kananaskis Centre for Environmental Research, employing highly advanced trace air pollutant monitoring procedures, were commissioned by Alberta Environment to demonstrate new technology for ambient air monitoring. Both studies reported many airborne trace organic compounds at a wide range of industrial sampling sites across Alberta. An expert committee of scientists reviewed the studies and the methods used in order to provide comments to the Minister of Environment concerning the merits and significance of the reports.

The methods are at the forefront of air monitoring technology. Such methods can provide a useful range of monitoring capabilities with the potential for sensitive and accurate identification and measurement of compounds. The studies indicated that a large number of substances can be found in almost any sample of air when state-of-the-art instruments are used to their maximum sensitivity. Neither study was intended to perform definitive identification or quantitative measurement of the many compounds observed. Both demonstrated the inherent ability of the methods to perform such measurements. Tentative identifications were made in many instances, but certain identities and accurate concentrations could only have been obtained by rigorous sampling and calibration procedures. Such procedures were outside the scope of the objectives for both studies.

Conclusive assessment of the data with regard to environmental quality or public health concerns was not possible since neither study was designed to provide a basis for such evaluation. Given the large

number of compounds tentatively identified, however, some commentary was deemed necessary.

An evaluation was done on the 14 compounds for which the reports provided some concentration estimates and for which industrial worker exposure limits were available. These showed that maximum airborne concentrations outside of industrial plant sites were generally less than 1/1000 of the statutory Alberta 8-hour occupational exposure limits. There have been no environmental health criteria set at such ultra-trace levels for these 14 compounds. On the basis of existing knowledge, adverse health effects would not be expected at such low levels.

The extraordinary sensitivity of the methods allowed tentative identification of many other compounds at ultra-trace levels. Health effects criteria are unavailable for most of these compounds at any level. Although health effects cannot be ruled out, the committee would not expect adverse health effects on the basis of the results reported by these two studies. These data, by their limited nature, are not capable of either supporting or resolving health complaints.

Overall, the committee believes that the contractors met the objectives of their studies and successfully demonstrated that these methods are capable of collecting accurate data which would be useful in comprehensive environmental studies.

TABLE OF CONTENTS

	Page
Executive Summary	ii
Table of Contents	iv
List of Tables	vi
List of Figures	vii
Expert Committee Members	viii
1. Introduction	1
1.1 Purpose of Studies	1
1.2 Need for Interpretation	4
1.3 Terms of Reference for Review Committee	4
1.4 Scope of Review	5
2. Critical Assessment of Methodologies	5
2.1 The TAGA 3000 Methodology	5
2.2 Adsorption Sampling - GC/MS Analysis	9
2.3 Comparison Between the TAGA 3000 and Adsorption Sampling - GC/MS Methods	11
2.3.1 Operation Principle	11
2.3.2 Response Time	12
2.3.3 Sensitivity and Sampling Requirements	12
2.3.4 Specificity in Identification	13
2.3.5 Quantitative Measurement	14
2.4 Summary	15

3. Critical Review of Reports. 16

3.1 Sciex Report 16

3.2 Kananaskis Report. 20

4. Significance of Findings. 21

4.1 Study Results in Relation to Objectives. 21

4.2 Analytical Significance of Survey Data 21

4.2.1 Qualitative Aspects 21

4.2.2 Quantitative Aspects. 23

4.2.3 Summary 24

4.3 General Considerations in Quantitative Analysis of Trace Compounds in the Atmosphere. 25

4.4 Possible Health Significance of Results. 27

4.4.1 Limitations to Interpretation of Results. . . 28

4.4.2 Health Effects Assessment. 29

4.5 General Meaning of High Sensitivity Analysis 33

5. Conclusions 40

BIBLIOGRAPHY. 42

APPENDIX 1 The Terms of Reference of the Contracts with Sciex, Inc. and Kananaskis Centre for Environmental Research. 43

APPENDIX 2 Data on Tenax and Chromosorb 101. 48

LIST OF TABLES

Page

1. Sampling Locations Selected for the Study Using the Sciex TAGA 3000 System 2

2. Sampling Locations Selected for the Study Using Kananaskis Centre's Adsorption Sampling - GC/MS System. 3

LIST OF FIGURES

Page

1. Normalized Concentration Range for Compounds for Which Quantitative Estimates and Health Criteria (8 hr. Occupational Exposure Limits, OEL) Exist 32
2. TAGA Mass Spectrum of Room Air Containing Cigarette Smoke. 34
3. TAGA Mass Spectrum of Breath of a Cigarette Smoker 35
4. TAGA Mass Spectrum of Typical Downtown Air in a Canadian (Non-Alberta) City 36
5. TAGA Mass Spectrum of Air in East Edmonton/County of Strathcona from the Present Survey 38
6. Relationship between Analytical Sensitivity and the Number of Compounds Identified in Different Samples. . . . 39

EXPERT COMMITTEE MEMBERS

Dr. Steve E. Hrudey is a professor in the Department of Civil Engineering at the University of Alberta. He holds a B.Sc. degree in Mechanical Engineering, M.Sc. and Ph.D. degrees in Public Health Engineering and is a licensed Professional Engineer in Alberta. Dr. Hrudey has published several articles and 3 book chapters covering air sampling and industrial water pollution control. In 1981-82 he conducted a field survey of hazardous waste treatment and disposal facilities in Europe and North America.

Dr. Byron G. Kratochvil is a professor in the Department of Chemistry at the University of Alberta. He holds a B.Sc. degree in chemical technology and M.Sc. and Ph.D. degrees in analytical chemistry. Dr. Kratochvil has published numerous articles and two books in the field of analytical chemistry. In 1980-81 he was guest scientist at the National Bureau of Standards, Washington, D.C. where he studied sampling in the Center for Analytical Chemistry.

Dr. John W. Markham is a physician and professor in the Department of Community Health Sciences at the University of Calgary. He holds a Bachelor of Medicine degree, a Bachelor of Surgery degree and a Fellowship of the Royal College of Physicians and Surgeons of Canada in Community Medicine. He has published work on health effects of potash dust and on the absorption of 2,4-D herbicide by sprayers. Dr. Markham is a member of the Department of National Health & Welfare Task Force on the Health Surveillance of Workers and President of the Alberta Occupational Health Society.

Dr. Robert R. Orford is Executive Director, Occupational Health Services of Alberta Workers' Health, Safety and Compensations. As well, he holds teaching positions at both the University of Alberta and the

University of Calgary. He holds an M.D., C.M., a M.Sc. in Internal Medicine, a Master of Public Health in Environmental and Occupational Health and Fellowships of the Royal College of Physicians and Surgeons of Canada in Internal Medicine and Community Medicine. Dr. Orford maintains an active interest in the health effects of air pollutants and is a member of the Provincial Board of Health and the Federal/Provincial Advisory Committee on Environmental and Occupational Health.

Dr. Ridley K. Shaw is a biochemist in the Biomedical Section at the Defence Research Establishment, Suffield. He holds a B.Sc. in Agriculture and M.Sc. and Ph.D. degrees in Biochemistry. He has 25 years of experience in specialized areas of toxicology and recent experience operating a TAGA system. Dr. Shaw is currently a member of the Pollution Study Group of the Public Advisory Committee under the Environment Council of Alberta.

1. INTRODUCTION

1.1 Purpose of Studies

In August and September 1981, the Air Quality Control Branch, Pollution Control Division of the Alberta Department of Environment commissioned two separate, but simultaneous studies for the purpose of demonstrating new technology for ambient air monitoring. The terms of reference of the relevant contracts are provided in Appendix 1.

The first of these studies involved the Sciex TAGA 3000 system, a single quadrupole mass spectrometer with an atmospheric pressure inlet system. This instrument has been developed for trace gas analysis. The major objective of the Sciex study was to assess qualitative capabilities of the TAGA unit, with almost instantaneous response, for atmospheric monitoring. Assessment of the instrument's quantitative capabilities was a lower priority. Consequently, many diverse industrial monitoring locations (Table 1) were selected, and Sciex Inc. was contracted to conduct demonstration surveys at these locations.

At the same time, the University of Calgary Kananaskis Centre for Environmental Research also contracted with Alberta Environment to conduct sampling at several of these locations (Table 2). The Kananaskis study used field sample collection onto adsorbents followed by gas chromatography/mass spectrometry (GC/MS) analysis in the laboratory. This study was intended to provide a comparison and reference for the TAGA demonstration.

Table 1 Sampling Locations Selected for the Study Using the Sciex TAGA 3000 System

Location	Number of Sampling Sites
Edmonton/Fort Saskatchewan/County of Strathcona	10
Atmore Compressor Station	4
Fort McMurray Area	18
Pincher Creek - Waterton Area	15
Princess Compressor Station	2
Hussar Compressor Station	3
Hussar Gas Plant	2
Cochrane	5
Calgary	5
Red Deer/Joffre Area	5

Table 2 Sampling Locations Selected for the Study Using Kananaskis Centre's Adsorption Sampling - GC/MS System

Location	Number of Sampling Sites
Fort Saskatchewan Area	2
Pincher Creek - Waterton Area	9
Cochrane	5

Neither study was designed nor intended to establish the public health or environmental significance of the data generated.

1.2 Need for Interpretation

As a result of these studies, a report was produced by each contractor. These two reports tentatively identified many organic compounds at various sampling locations.

Because of the newness of the TAGA technology and the high sensitivity for compound detection of both techniques, the data generated lay significantly beyond existing air quality information for Alberta or most other regions in the industrialized world. Consequently, the Minister of Environment established an expert committee to review the findings contained in these two reports to provide a reasonable basis for their interpretation and use by the Department and other interested parties.

1.3 Terms of Reference for Review Committee

The four major undertakings of the Committee were to:

1. Review the two methods and document their sensitivities, interferences, sample decomposition/reactions, accuracy, etc.
2. Indicate the confidence which should be placed on the specific compound identifications and concentrations reported.
3. Provide comments as to the merits and significance of the reports to the Minister.

4. Submit a final report to the Minister within two months of the Committee formation.

1.4 Scope of Review

The two reports provide a large amount of data derived from application of the specific methods. Review of these data involved three major facets:

1. The strengths and weaknesses of the specific analytical methods.
2. The manner in which the data have been presented and summarized by the reports.
3. The possible significance of the data in relation to current knowledge of environmental quality and public health protection.

2. CRITICAL ASSESSMENT OF METHODOLOGIES

2.1 The TAGA 3000 Methodology

The TAGA 3000 instrument identifies and measures trace gases by means of a quadrupole mass spectrometer. The technology for this type of spectrometer is well-known. The major feature of the TAGA 3000 is that it provides a special direct air-sampling source which allows air to be sampled and analyzed on a continuous basis. Water or oxygen in the air is used as a reagent to convert the trace gases to species that can be detected by the instrument. Particulate matter in the air, either solid or liquid, is not sampled.

The TAGA 3000 instrument is rugged and portable.

Considerable attention has been devoted to making the unit insensitive to vibration and jarring. This feature allows it to operate in a vehicle for both sampling and analysis purposes, even while in motion. As a result, almost instantaneous, continuous profiling is possible for stack plumes, general emissions from industrial sites and other dynamic phenomena.

To be detected in a mass spectrometer such as the TAGA 3000, a gas molecule must take on a positive or negative charge. This is accomplished in the TAGA 3000 by collision with ions produced in the instrument.

Some trace gases react selectively with ions produced from water, others with ions produced from oxygen. The instrument cannot measure both types simultaneously but can be switched rapidly from one mode to the other (within a minute). With water as the ionization reagent, the system is most sensitive to organic molecules containing oxygen in the form of alcohols, ketones and esters. With oxygen as reagent, sensitivity is greatest for sulphur dioxide, nitrogen oxides, aldehydes, phenols and carboxylic acids. By introducing other reagents into the system, additional classes of compounds are more readily detected and measured. For example, benzene increases the sensitivity of the system to aromatic and polynuclear aromatic hydrocarbons. Also, use of a photolysis pre-reactor enhances the sensitivity to sulphur compounds such as thiols, thioethers and disulphides.

A preliminary gas chromatographic separation can be introduced ahead of the TAGA, just as it is used ahead of the

mass spectrometer in the Kananaskis GC/MS approach. When used in this mode, the TAGA 3000 system differs little from the conventional GC/MS.

The TAGA instrument can be used for both qualitative and quantitative analysis. In the qualitative mode, the identity of a compound must be inferred from: (a) mass-to-charge ratio of the ions produced, which are related to the molecular weight of the compounds; (b) operating mode in use; (c) chemical knowledge of the operator; and (d) knowledge of the types of compounds likely to be present on the basis of sample origin. A computer searchable reference data base can be used to aid in identification, but the data base provides only a tabulation of compounds according to molecular weight. Even with a sound knowledge of ion-molecule reactions, identification may be difficult. Also, interference of different trace pollutants with each other is possible when identification is attempted without prior compound separation. However, an experienced operator can usually narrow the possibilities and make reasonable predictions based on the factors mentioned above.

The TAGA system is highly sensitive. Many compounds can be detected at the part per billion level and quite a few at parts per trillion. (For reference, 1 part per billion is the equivalent of 1 second in 31.7 years; 1 part per trillion, 1 second in 317 centuries.) Such sensitivity allows detection of many compounds at concentrations well below levels at which health effects have been documented. Obtaining this sensitivity for different classes of compounds may require

repetition of measurements in different modes with different chemical ionization reagents. To obtain statistically reliable results, direct sampling and measurement must usually be carried out for about 1/2 hour for each site. Under these conditions, averaging of separate sample results by the TAGA system is comparable to integrated sample averaging in other techniques, such as the adsorption GC/MS method. Only semi-quantitative data can be obtained when the TAGA is being used in the scanning mode to search for compounds. However, real-time analysis can provide useful quantitative information when the instrument is in the single ion mode and only a few specific ion peaks are being monitored. Once the relevant ions have been found, up to eight ions can be simultaneously measured in real-time.

Presence in the sample of any substance that gives a background signal at the same mass-to-charge ratio constitutes a chemical interference, and the signal for the compound of interest must be measured on top of this background. Interferences of this kind may significantly reduce the sensitivity of the measurement.

2.2 Adsorption Sampling - GC/MS Analysis

The analytical method used by the Kananaskis Centre involves the trapping of trace substances on the surface of two adsorbents, Tenax GC polymer beads and Chromosorb 101. The samples were collected by first drawing air through a glass tube containing the Tenax beads, then through a second tube containing the Chromosorb 101. (See Appendix 2 for data on adsorbents.) Sampling rates of 100 to 150 mL/min and sampling times of 10 min to 2 hr were used. The tubes containing the adsorbed compounds were then transported to the laboratory.

The tubes were kept at 0 to 3°C until analyzed. The more volatile components were introduced into the gas chromatograph by heating the tubes to 250°C, while purging with helium at 50 mL/min. Less volatile materials were extracted from the adsorbents with pure n-hexane, which was syringe-injected into the gas chromatograph.

The sampling operations used are typical for trace air pollution studies. Separation in time of the sampling and analysis steps is advantageous because the instrument is not tied to a particular location, and the analytical measurements need not be done until the instrument is performing at optimum conditions. Potential problems with this system include uncertain collection efficiency on the adsorbents, instability of the adsorbed compounds and adsorbent, and incompleteness of recovery of the adsorbed compounds for analysis. Collection efficiency depends on the nature of the adsorbent, the nature and concentrations of the sample compounds and the collection

time and temperature. Some gases do not adsorb as readily as others. Also, high concentrations of strongly adsorbing substances may saturate the adsorption sites, displacing more weakly adsorbing compounds.

Tenax GC and Chromosorb 101 are frequently used as adsorbents because most types of organic compounds are at least partially adsorbed by these materials. As noted in the Kananaskis report, accurate measurement requires care to avoid exceeding the capacity of the sample tubes. Additional studies would be needed to insure that this did not occur. Little information is available on possible sample loss or reaction during transportation. Use of low temperature storage should aid, however, in reducing loss and decomposition.

Particulate material in the atmosphere is likely to be retained by the Tenax and Chromosorb columns through a filtering effect unless pre-filters are installed ahead of the adsorber columns. This means that those compounds which tend to adsorb on particles, such as polynuclear aromatic hydrocarbons on lead oxide particulates, are trapped and would be measured by this system. More studies would be needed to establish the quantitative capabilities of these two adsorbents for those compounds of interest to Alberta Environment.

Identification of the compounds eluted from the adsorbent into the GC/MS instrument can be carried out by: (a) computer matching electron impact mass spectra with library spectra; (b) comparing retention volume (retention time) in gas chromatograms; and (c) examining fragmentation patterns when computer matches are weak. Potential problems with compound identification include: (a) incomplete gas chromatographic separation causing the introduction of two or more compounds into the mass spectrometer at the same retention volume; (b) incomplete libraries of mass spectra; and (c) variations in library data because of different instruments and conditions.

2.3 Comparison between the TAGA 3000 and Adsorption Sampling - GC/MS Methods

2.3.1 Operation Principle

Both techniques use a mass spectrometer to detect, identify and measure organic components in air. The TAGA 3000 uses chemical ionization, GC/MS uses electron impact ionization. Chemical ionization provides selectivity and high sensitivity but little specificity. Electron impact ionization provides high specificity, in the form of fragmentation patterns produced, but generally lower sensitivity and poor selectivity. As a result, preliminary separation of sample components by a gas chromatograph is required for mass spectrometric identification. On the other hand, the selectivity of chemical ionization in the TAGA 3000 system makes preliminary separation less important.

2.3.2 Response Time

Mass spectrometric response is effectively instantaneous; the time between sample introduction and measurement is of the order of milliseconds. Therefore, the mobile TAGA 3000 is useful as a plume tracking device or a continuous monitor in either the single-ion or multiple-ion monitoring mode provided only one ionization mode is required for all compounds of interest. Gas chromatographic separation requires injection of a discrete sample, which is followed by the sequential appearance of individual components over a period of seconds or minutes. Therefore, the instantaneous response of the mass spectrometer is lost when GC and MS are used together.

2.3.3 Sensitivity and Sampling Requirements

Because of the lower sensitivity of electron impact ionization and the non-continuous nature of GC/MS, compounds present at trace levels must be collected and concentrated, usually onto an adsorbent, before analysis. This sampling step raises questions about adsorption and desorption efficiencies as well as possible decomposition of samples or adsorbents with time. Incomplete collection may be the reason why the adsorption sampling - GC/MS method seems to be "insensitive" to the small polar organic molecules detected by the TAGA. On the other hand, the direct sampling system of a TAGA 3000 involves a curtain of gas to deflect all particulates in the sample from the entrance port. Therefore, all sample components which exist as, or are

attached to, aerosols or particulates are not detected. This may explain why the TAGA 3000 seems to "miss" some high molecular weight compounds that are seen by the GC/MS technique.

2.3.4. Specificity in Identification

For the adsorption sampling - GC/MS system, electron impact ionization gives "finger-print" fragmentation patterns, which are characteristic of individual compounds. The only requirement for reliable identification is adequate separation by the gas chromatograph so that specificity is not impaired by the presence of fragments from other compounds. Confirmation can be made by running known standards under the same conditions.

The chemical ionization mass spectra obtained with the TAGA 3000 offer little specificity. Typically, quasi-molecular ions are produced that are related to the molecular weight of the parent compounds. Identification depends on the selectivity inherent in different chemical ionization modes. That is, many possible interfering compounds are not seen because they are not ionized in certain modes. However, positive identification may not be possible, even by running known standards under the same conditions, because different compounds may yield the same ion peak. This lack of specificity toward different compounds with the same molecular weight is a limitation of chemical ionization.

As a result, effective use of the TAGA 3000 depends heavily on the operator's knowledge of ion-molecule reactions. The adsorption sampling-GC/MS method has fewer variables to consider. Interpretation of mass spectra produced by GC/MS can be aided by computer matching, but even here interpretation by an experienced mass spectroscopist is indispensable in many cases.

2.3.5 Quantitative Measurement

Quantitative analysis with both the TAGA 3000 and the GC/MS, as with any analytical method, requires calibration using reference standards. This involves careful introduction of small amounts of pure substances or use of standard reference gas mixtures. A calibration procedure must be performed on each compound to be measured.

Ion generation, ion transmission and ion detection inside a mass spectrometer are sensitive to day-to-day variation. The TAGA 3000 provides more reproducible ion generation because reagent ions are always in such large excess that fluctuations in ion generation are not important. The sensitivity of the TAGA 3000 toward a given compound may depend, however, on the other species present in the sample. Therefore, calibrations for the TAGA 3000 should be done in the field. Calibrations for the GC/MS method should be done as close to the time of sample analysis as possible. For ion detection, an ion counting method such as used in the TAGA 3000 gives improved precision over conventional current-measuring devices for ion detection.

2.4 Summary

The best methods for identification and measurement of trace substances in the atmosphere are the relatively new direct sampling and measurement system of the TAGA instrument and the more conventional method of collection on an adsorbent, followed by analysis in a laboratory by combined gas chromatography and mass spectrometry (GC/MS). More recent advances, such as the TAGA 6000, extend the analytical capability well beyond that available for these studies and overcome some of the limitations described. Such advances are considered to be extensions of the basic methods rather than alternative methods.

The TAGA 3000 mass spectrometer provides real-time instantaneous analyses of most trace gaseous components in the atmosphere. It can be mounted in a large van to measure fugitive emissions directly from plants or gas wells, to track stack plumes, and so on. For both methods, accurate identification and measurement of unknown trace compounds requires computer library scanning and evaluation by knowledgeable, experienced operators. Furthermore, accurate measurement requires careful calibration with pure standards. The GC/MS system used by the Kananaskis Research Centre traps trace compounds by drawing air for a few minutes to a few hours through adsorbent tubes. The adsorbed substances are later desorbed into a gas chromatographic separation unit, followed directly by analysis in a mass spectrometer. The TAGA method is fast, sensitive, and expensive. The adsorption

GC/MS method is slower but allows flexible sampling and is less costly.

3. CRITICAL REVIEW OF REPORTS

3.1 Sciex Report

The report emphasizes that the short time provided for the required work imposed limitations on what could be accomplished (p.4 Sciex report). Ideally, a survey carried out using the TAGA 3000 would include a list of the most likely compounds to be encountered, based upon a knowledge of the industrial processes being monitored.

The Sciex report provided only a summary of the compounds tentatively identified using positive and negative ion modes. The degrees of confidence in the identifications were not given. Since identification is based on six different factors (p. 17, Sciex report), some of which require extensive TAGA operating experience, it is impossible for readers of the report to independently estimate the uncertainty in the identifications. Had the report provided confidence data, perhaps on a four or five point scale ranging from high confidence through moderate to low confidence, the reader would have some basis for interpreting the results.

Although quantitative data were not specifically requested for all compounds detected, some indication of amounts present would have been valuable. The lack of quantitative calibration data for different compounds makes it

impossible to generally correlate ion count values with concentrations because sensitivities can vary by as much as four orders of magnitude (Appendix I, Sciex report).

Given the extreme sensitivity of the instrument, the report could have attempted to highlight those compounds which are clearly of higher concentration. This could have been done by including additional data tabulations with ion count cutoffs higher than the 1000 counts per second used in the report. For example, as an approximation, compounds with more than 10,000 ion counts per second should be present at concentrations of between 0.0002 to 2 parts per million. Compounds with more than 100,000 ion counts per second would normally correspond to concentrations of 0.002 to 20 parts per million. Using higher ion count cutoffs would provide a smaller, more manageable, data base for further assessment. Compounds of lower sensitivity would be missed in such a data set, but the perspective provided by using higher ion count cutoffs would be useful.

The authors indicated in two instances that they were able to make a more reliable identification of a compound than was normally possible. In the first instance, aldehydes and ketones were separated one from the other by taking advantage of clustering phenomena (p. 17, Sciex report); in the second, hydrogen fluoride was positively identified by employing high fragmentation potentials (p. 19, Sciex report).

The discussion (pp. 18-61, Sciex report) provides little more than a brief summary of some of the data collected. Only

when reference is made to the appendices (Sciex report) does it become apparent that many of the sites exhibit many more compounds than were discussed. These should have been more clearly described. Furthermore, interpretation of the appendices (Sciex report) is very difficult since neither site maps, showing sampling locations, nor meteorological information are provided.

Some of the identifications assigned to various masses appear inappropriate. For example, in Appendix 5 under negative ions, the assignment of succinic acid for mass 117 in the Pincher Creek area is improbable. An example of a more acceptable statement appears on page 27, "..... a decrease in benzene at m/z = 78 was not accompanied by an increase in the specified pollutants .... This is indicative of the existence of other aromatic components than alkylbenzenes and naphthalenes."

In addition, the following specific comments apply to the Sciex report.

1. On the first line of p. 3 and again on the last line of p. 15, the report states that each scan represents an average of at least three samples. Since air is flowing into the TAGA 3000 continuously, the concept of discrete samples is misleading; each scan is obtained by averaging three multi-ion scans for better statistical results.
2. On p. 3, the detection limit for nitrogen oxides should be 5 ppt, not 5 ppb. The report should note that the detection limits listed are obtained by assuming a

baseline noise of 10 ion counts per second and a detection limit corresponding to 3 times the noise level.

3. On p. 12, the second paragraph describes the calibration method for liquid compounds. None of the four compounds calibrated, however, are liquids. SO_2 and NO_x are gases, while phenol and naphthalene are solids at room temperature. It would have been appropriate to describe in more detail how both solid and gaseous compounds are calibrated.
4. The first line of p. 19 states that methyl ethyl ketone (MW=72) is identified according to figure 4.4.1-2 (p. 21). In the figures, the mass-to-charge ratio identified as methyl ethyl ketone is 75, corresponding to MW=74. The latter statement is incorrect.
5. In Appendix 5, the site #2 description should read "600 yards from Waterton...", not "600 miles...."
6. Errors occur in the master tabulations of compounds identified (Appendices 2 to 11). For example, phenol was observed in Cochrane areas according to the text of the report and the raw data, but was not marked as a compound identified in Appendix 9 b (Cochrane) of the master tabulation.

3.2 Kananaskis Report

The report indicates that both gas chromatographic retention volumes and computer-matched spectral search results were used to identify compounds (p. 9 Kananaskis report). However, information as to which compounds were identified only by mass spectra data, and which by a combination of mass spectral fragmentation data and gas chromatographic elution times, was not included in the report. This additional information is necessary to assess the confidence in the identification of those compounds for which standards were not run.

The sampling system used by Kananaskis employed a "personal" sampling pump to draw air through the two adsorbent tubes. Both sorbents were said to have been preconditioned. Details of the preconditioning, along with the sorbent column dimensions, should have been provided since pretreatment and column size could have a significant effect on results obtained.

Sampling rates (100 to 150 mL/min) and sample collection times (10 min to 2 hr) should have been specified for each data set so that overall sample volumes could be estimated. The times from sample collection to analysis should also have been given.

The Kananaskis report did not provide information on what information other than computer searches of mass spectral data libraries was used to identify the compounds reported. As

well, this report did not contain a summary of results, nor did it discuss the limitations of the method.

4. SIGNIFICANCE OF FINDINGS

4.1 Study Results in Relation to Objectives

Both studies were aimed at demonstrating the capabilities of the respective methods. In neither case was quantitative information specified as a primary objective of the studies. In this context, the study objectives were met since a useful field evaluation of the abilities and limitations of the two methods was achieved.

The TAGA 3000 demonstrated an ability to remain operational under very rigorous travel conditions. The adsorption GC/MS system was found to be reasonably flexible in application.

Despite the limited scope of the objectives, data gathered from these surveys did provide an important basis for the issuance of Control Orders under the Clean Air Act.

4.2 Analytical Significance of Survey Data

4.2.1 Qualitative Aspects

In accordance with the terms of reference, both systems were used primarily as qualitative detectors of trace atmospheric gases at several locations in Alberta. Because the systems are extremely sensitive to many (but not all) compounds that might be present, an extremely large number of substances were observed. Under the conditions of the study, the identification of these substances was, for the most part, tentative.

In some cases, the two reports tentatively identified different compounds for the same molecular weight. Examples from data near Alberta Food Products include diethylmethylbenzene (mol. wt. 148 p. 10, Table 2 of Kananaskis Report est. 6.2 ug/m^3) and phthalic anhydride (p. 2 of App. 2a of Sciex Report). Likewise, methylcyclopentane (mol. wt. 84 p.10, Table 2 of Kananaskis Report est. 18 ug/m^3) and cyclopentanone (p. 1 of App. 2a of Sciex Report) were alternately proposed.

For some sites, one method identified compounds not found by the other. Examples, again from data near Alberta Food Products, include identification and measurement by Kananaskis of naphthalene and phenol. These compounds, although found at other sites by Sciex, were not reported for the Alberta Food Products location. At this site, Sciex identified ethylene glycol (mol. wt. 62) and a 4-carbon amine or dimethylformamide (mol. wt.73), which were not observed by Kananaskis. In general, Kananaskis identified many alkyl and aromatic hydrocarbons that were not seen by Sciex, while Sciex reported the presence of many heterocyclic compounds not observed by Kananaskis.

The TAGA 3000 likely missed the nonpolar hydrocarbons because of not being equipped with the recently developed "reduced pressure ionization source". This source would provide increased sensitivity for such molecules. It would also provide the capability to detect low levels of vinyl chloride monomer. This source was not available for the Alberta study. Conversion from an atmospheric pressure to a

reduced pressure inlet system requires several hours. This is a disadvantage in mobile monitoring if both hydrocarbons and heterocyclic compounds are of interest.

The failure of adsorption - GC/MS to observe many of the heterocyclic compounds seen by the TAGA 3000 may mean that they were not trapped by the adsorbents. Perhaps more likely, they may have been present in such extremely low concentrations that they were below the limits of detection of the adsorption - GC/MS procedure.

These comments are directed at the detection of substances at extraordinarily low levels and are mentioned to indicate that careful study is needed to verify the presence of specific compounds at trace levels.

Another limitation of the studies, as defined by their terms of reference, was the shortage of background data. As a result, compounds reported present at a particular site may not have originated from the industry in that area.

4.2.2 Quantitative Aspects

Variability in the trace organic composition of the atmosphere near point sources is likely to be so great that obtaining meaningful quantitative data would require measurements over a period of minutes to hours. Sampling is by far the greatest source of uncertainty in estimating quantities of compounds present. Quantitative measurements with even a precision of ±100% at the part per billion level or lower would require measurements integrated over sufficient time that atmospheric eddy effects could be averaged out.

Required sampling time could be determined for each site, but would require a protocol to evaluate the extent of such variability in the series of measurements.

Comparison of any quantitative results by the two methods may not be meaningful. The TAGA 3000 gives instantaneous readings or short "time-average" readings. Adsorption - GC/MS provides longer (10 minutes to 2 hours) "time-average" readings. Any direct comparison is affected by the variability of the emission source and of the corresponding plume.

An example of the differences that can be observed occurs in the findings for the Cochrane area. Both methods reported concentrations of around 0.001 ppm phenol and 0.010 ppm naphthalene on the main street as well as in an area adjacent to and downwind of the wood treatment plant. At a site on the plant property, parallel to a train carrying treated wood, the adsorption sampling - GC/MS method registered 0.125 ppm phenol and 16 ppm naphthalene. Readings of only 0.020 ppm phenol and 0.030 ppm naphthalene were measured by the TAGA 3000 at one instant within the sampling period of the adsorption - GC/MS method. This large difference illustrates the great variability inherent in short-term air sampling. Such variability must be considered when trying to assess sample significance.

4.2.3 Summary

In general, both reports listed many substances present at trace levels. The Kananaskis report identified a number of

hydrocarbons that were not reported by Sciex. On the other hand, the Sciex report listed a number of nitrogen, oxygen and sulfur-containing compounds that were not reported by Kananaskis. Additional work could clear up the small number of discrepancies. The highly variable distribution of trace compounds in the atmosphere requires extensive sampling if accurate measurement is required.

4.3 General Considerations in Quantitative Analysis of Trace Compounds in the Atmosphere

For environmental measurements to be useful in decision-making they must be sufficiently accurate to provide valid answers to relevant questions. With trace organic compounds in particular, the levels may be so low, and the number of compounds so large, that precise and accurate measurement may be time-consuming and expensive. Accordingly, it is important to decide beforehand what compounds or classes of compounds are to be investigated and what level of analytical precision is necessary. The precision of the results depends primarily on sampling and analytical methodology. Specifically, the number, size, location, frequency and quality of the samples, and the precision and accuracy of the analytical methods are important.

Sampling is expensive and time-consuming. Analytical results are meaningless for interpreting air quality if the samples from which they are obtained are not adequately representative of the environment to be studied. The heterogeneity of most environmental systems usually requires a

large number of samples. If an average concentration is adequate, the samples may be combined and a few subsamples analyzed from the blended composite sample. This may save analytical time and effort. But if the variability of the system must be known, then many individual samples must be analyzed. The samples should be collected, stored and transported to the laboratory according to a well defined protocol that accounts for the known effects of time and storage conditions on sample quality. Real-time analysis with the TAGA overcomes most sample handling problems, although this flexibility is limited to a single chemical ionization mode at any given time.

The analytical measurements should be made using a properly tested procedure with adequate calibrations and controls. The method must be checked frequently during use by analyzing standards and samples spiked with known amounts of the compound under test. The American Chemical Society Committee on Environmental Analytical Chemistry (Analytical Chemistry 52, 2242 (1980)) recommends that data be obtained, whenever possible, from calibration standards, field blanks, spiked field blanks, spiked laboratory blanks, working standards and field samples.

Measurement is evaluated by the precision and accuracy of the results; if the data are precise, random error is low, and if accurate, systematic error is low. Care must also be taken in handling the data. Electronic data collection and storage systems can save time and reduce errors but should be checked regularly with known data. Results must be calculated correctly and reported with the appropriate number of

significant figures. An estimate of the uncertainty in the reported values should be provided, preferably as standard deviation. Finally, the procedures used for sampling, sample handling, sample pretreatment, analysis and data handling should be thoroughly documented so that all steps of the procedure can be evaluated. Ultimately, the level of the target component may be below the limit of measurement of a method, but it can still be detectable. Under such circumstances useful qualitative information can often be attained.

In summary, the reliable collection of quantitative environmental data can only result from a well planned and carefully executed program. This must be developed with the specific intention of acquiring quantitative rather than qualitative data.

4.4 Possible Health Significance of Results

The committee considered if the results in the Sciex and Kananaskis reports provided reliable new knowledge concerning human health in relation to airborne environmental contaminants at the sites studied.

For this to be achieved, it would first have been necessary to obtain relevant information concerning the exposure and dosage of a human population or individual to the chemical or chemicals in question. This would have required the use of sampling methods which would have given a reasonably representative exposure profile over time together with accurate chemical identification.

Recording of other exposures and health factors of importance would also have been needed for individuals or a representative sample of the exposed population. The Sciex and Kananaskis studies were not designed to meet these requirements. Therefore, the fundamental basis for determining an exposure/effect or dose/response relationship was not provided by either study.

4.4.1 Limitations to Interpretation of Results

Sound scientific practice precludes drawing firm conclusions about the effects of a given factor when it is known that the data are not suitable for that purpose. However, because of the number and variety of compounds detected, the committee concluded that some commentary was necessary, no matter how weak the basis.

The limitations to a health effects assessment of the data in these reports include the following:

i) The limited sampling could not truly represent environmental levels of individual compounds.

ii) The degree of confidence in the identification of individual compounds is variable at the low levels observed.

iii) The amount of quantitative data is limited.

iv) The accuracy and precision of the analytical measurement is uncertain.

v) Knowledge of health effects at extremely low levels, for those pollutants with known health effects at higher levels, is unavailable.

vi) Knowledge of health effects at any level is unavailable for many of the compounds tentatively identified.

4.4.2 Health Effects Assessment

Target organisms may be exposed to airborne substances by various routes. Some substances may be inhaled, and some may be absorbed through other routes (eg. skin, ingestion). The effects which a substance produces in the human are variable, depending on the individual's susceptibility, dose/response relationship and other toxicological factors. The effect produced may be either acute or chronic.

Through experience, both experimental and epidemiological, acquired evidence allows establishment of "standards" for human or animal exposure limits. In occupational health, these standards are referred to as occupational exposure limits, or threshold limit values. These are concentrations to which nearly all workers may be exposed without adverse health effects. The levels vary somewhat, depending on the length of exposure. Time frames of 8 hours, 15 minutes and instantaneous are normally used. However, public exposure is not limited to working hours but may continue over a long time. Also, the public contains a spectrum of ages and health conditions.

In addition to the occupational standards, a more limited number of environmental exposure limits have been established for some compounds (e.g. ozone and carbon monoxide). These are generally an order of magnitude (factor of 10) or more below the occupational exposure limits and cover time spans

ranging from one hour to one year, assuming continuous exposure. Such limits are intended to protect the general population, including all age groups.

At one tenth of the occupational exposure level, concentrations are usually still at the parts per million rather than the parts per billion or parts per trillion levels observed for most of the compounds identified in this study. These substantially lower levels have not generally been known to represent significant hazards to human health, although relatively few compounds have been evaluated at low levels. Caution must be taken in the medical or biological interpretation of low level exposures if genotoxic factors are significant.

Many environmental exposure limits are based on criteria other than human health, where such alternate criteria are more sensitive. For example, sulphur dioxide limits are based on vegetation damage and hydrogen sulphide limits are based on odor because these factors are affected at concentrations lower than those which are commonly believed necessary to produce significant health effects. Environmental exposure limits have been set for relatively few compounds anywhere in the world.

Faced with the severe practical limitations identified in 4.4.1, an assessment of health significance associated with the data reported must rely on what is known about pollutants for which health effects have been established. Of all the compounds tentatively identified, only 14 had both

quantitative estimates and specified occupational exposure limits. Of these, 13 were measured by GC/MS and 3 by TAGA.

To provide some understanding of how the estimated atmospheric levels compare with allowable occupational exposures, the ratios of the former to the latter are plotted in Figure 1 for the 14 compounds. The range of ratios is indicated for each compound considering all the sites for which such data were available. The scale is compressed by using logarithms since a range of two hundred million had to be covered. The legend on Figure 1 distinguishes the methods and whether the levels were measured on public land or on industrial plant property.

Most of the ratios are less than one one-thousandth of the 8-hour occupational exposure limit. The only exceptions are the high levels of naphthalene, phenol and cresol (components of creosote, or coal tar) identified close to freshly treated wood on an industrial plant site. This particular situation led to the issuance of an Emission Control Order by Alberta Environment.

The sulphur dioxide results in Figure 1 require explanation. The higher readings, including the highest concentration of 0.140 ppm (equivalent to 0.07 of the 8-hour occupational exposure limit), were measured by TAGA 3000 during plume tracking (pp. 20, 29, 36 and 37, Sciex report). These SO_2 concentrations are instantaneous values measured in the plumes. They should not be confused with time-averaged

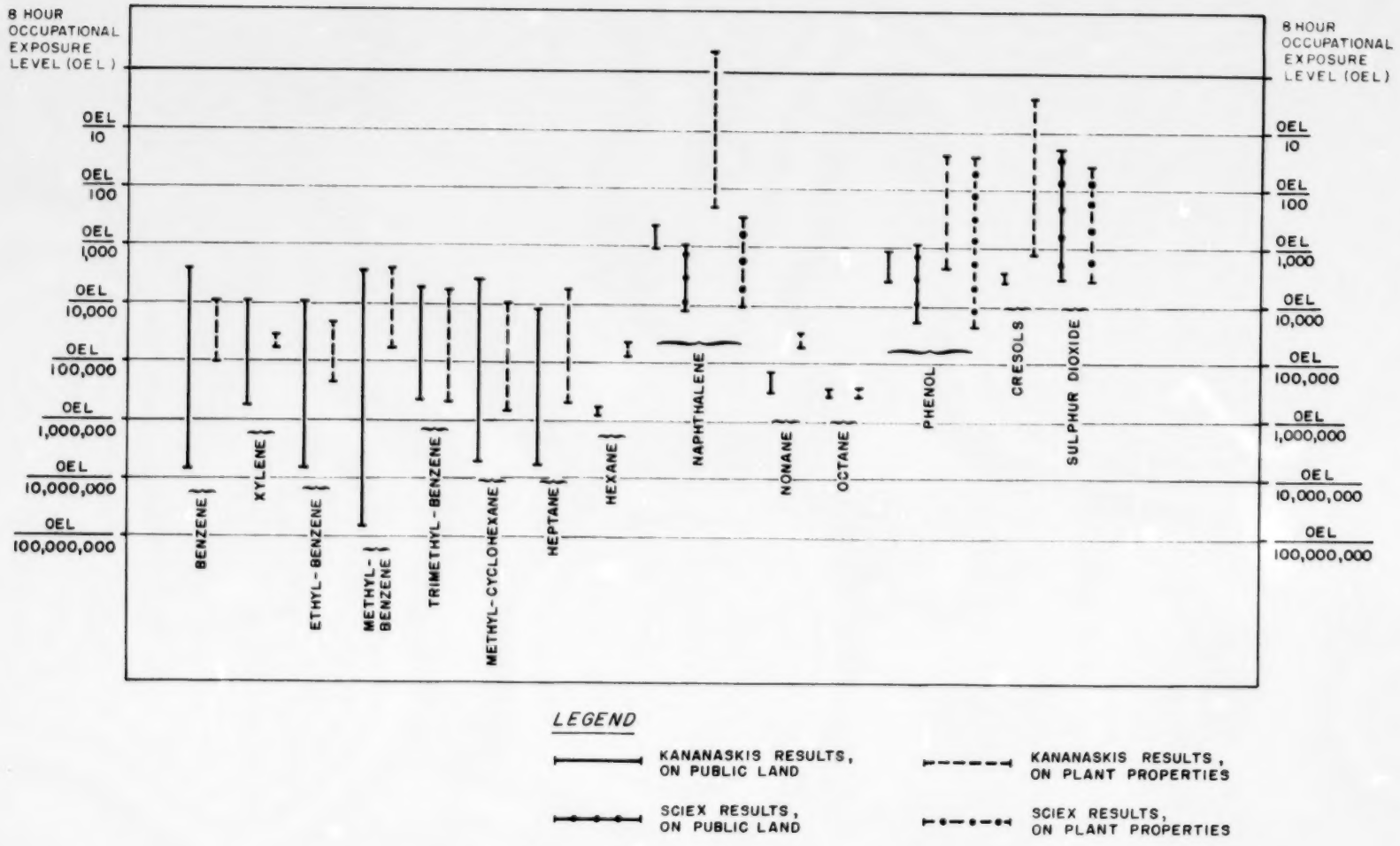


FIGURE I. NORMALIZED CONCENTRATION RANGE FOR COMPOUNDS FOR WHICH QUANTITATIVE ESTIMATES AND HEALTH CRITERIA (8 hr. Occupational Exposure Limits, OEL) EXIST.

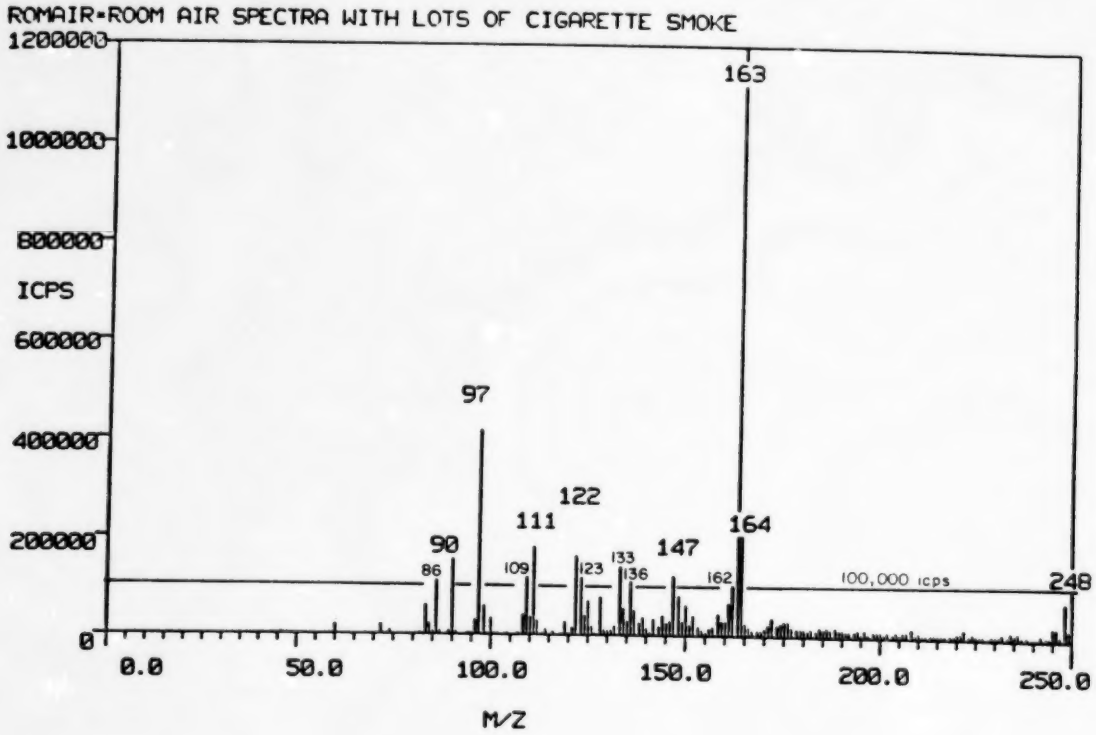
stationary values which will be much lower than these peak values.

In summary, at the public sites where there were no reports of adverse health effects, these data do not suggest that health effects should be expected. Where complaints of health effects attributed to air pollution do exist, the trace concentrations detected may or may not be relevant. Present scientific criteria for environmental health effects of trace contaminants are either inadequately defined or unavailable in most cases. The finding of trace concentrations of potentially noxious compounds at a location where serious, unresolved health complaints occur would be grounds for a detailed investigation. However, on the basis of current knowledge of air pollution health effects and the data reported in these two studies, with their limitations, adverse health effects would not be anticipated.

4.5. General Meaning of High Sensitivity Analysis

For some people, tentative identification of any compounds in the atmosphere may pose a concern. Such concern must be balanced with the knowledge that, given the high analytical sensitivity of the methods now available, the identification of many compounds in almost any sample of air is likely. This reality may be appreciated by looking at the wide range of organic compounds found in most atmospheres.

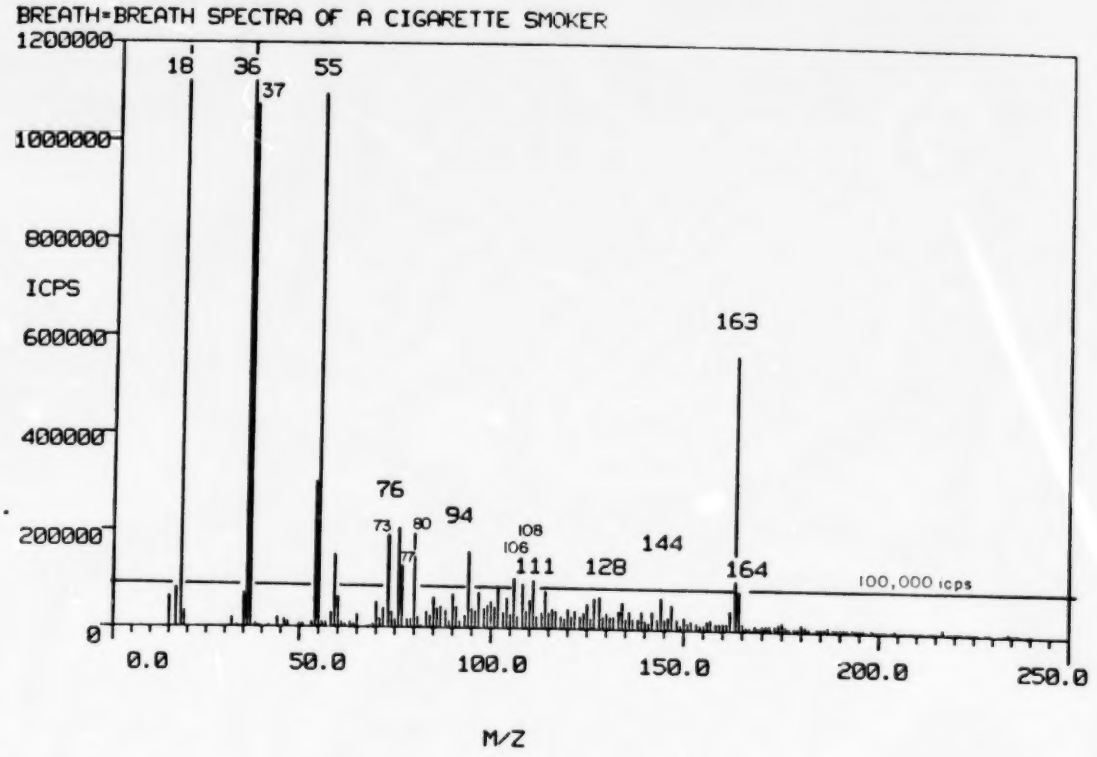
For comparison, Figures 2 to 4 show TAGA air spectra for room air with cigarette smoke, breath from a cigarette smoker and downtown air in a Canadian city outside Alberta. Figure 4



Assignments of mass-to-charge ratio (m/z) for peaks exceeding 100,000 counts/s:

m/z	assignment	m/z	assignment
86	cyclopentanone	123	dimethylphenol; phenylethanol; benzoic acid
90	a hydroxylamine	133	methylbenzofuran; cinnamaldehyde
97	dimethylfuran; dimethylpyrazol	136	benzothiazole
109	amino-methylpyridine; cresols; anisole; benzyl alcohol	147	unidentified
111	hydroquinone, resorcinol	162	nicotine
122	alkylated pyridine	163	nicotine
		164	nicotine

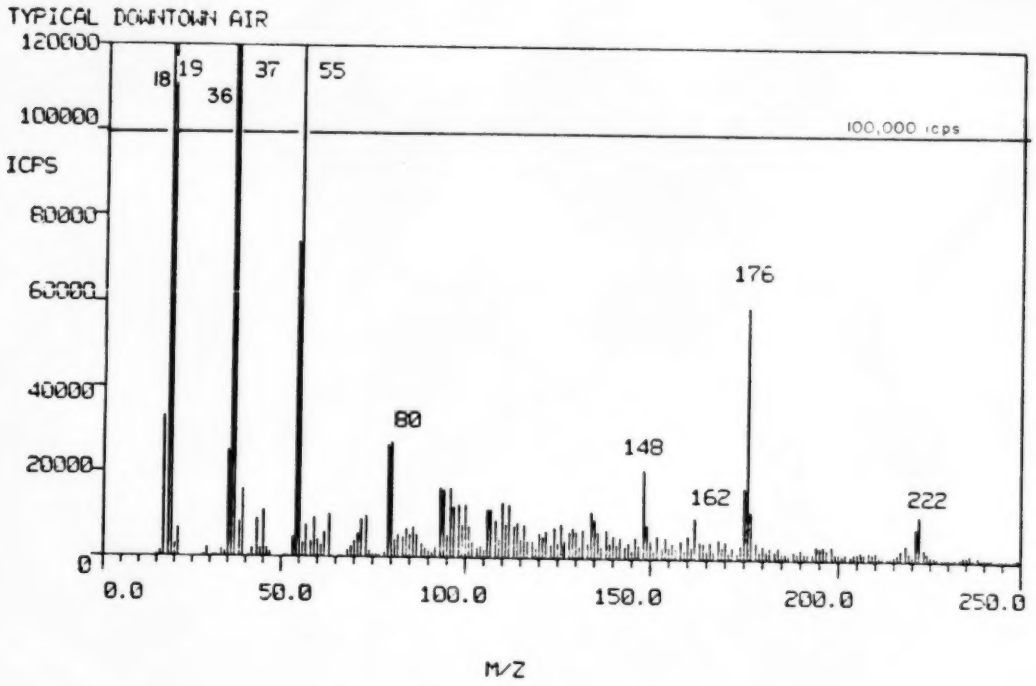
Figure 2 TAGA Mass Spectrum of Room Air Containing Cigarette Smoke (provided by Sciex, Inc.)



Assignments of mass-to-charge ratio (m/z) for peaks exceeding 100,000 counts/s:

m/z	assignment	m/z	assignment
18	ammonia	106	diethanolamine
36	ammonia	108	ethylpyridine; methylaniline; benzylamine
37	water		
55	water		
73	water	111	hydroquinone; resorcinol
76	a hydroxylamine		
77	trimethylene glycol; propylene glycol	128	N-ethylcyclohexylamine; N,N-dimethylcyclohexylamine;
80	pyridine	144	methylquinoline
94	picoline	163	nicotine

Figure 3 TAGA Mass Spectrum of Breath of a Cigarette Smoker (provided by Sciex, Inc.)



Assignments of mass-to-charge ratio (m/z) for peaks exceeding 100,000 counts/s:

m/z	assignment	m/z	assignment
18	ammonia	37	water
19	water	55	water
36	ammonia		

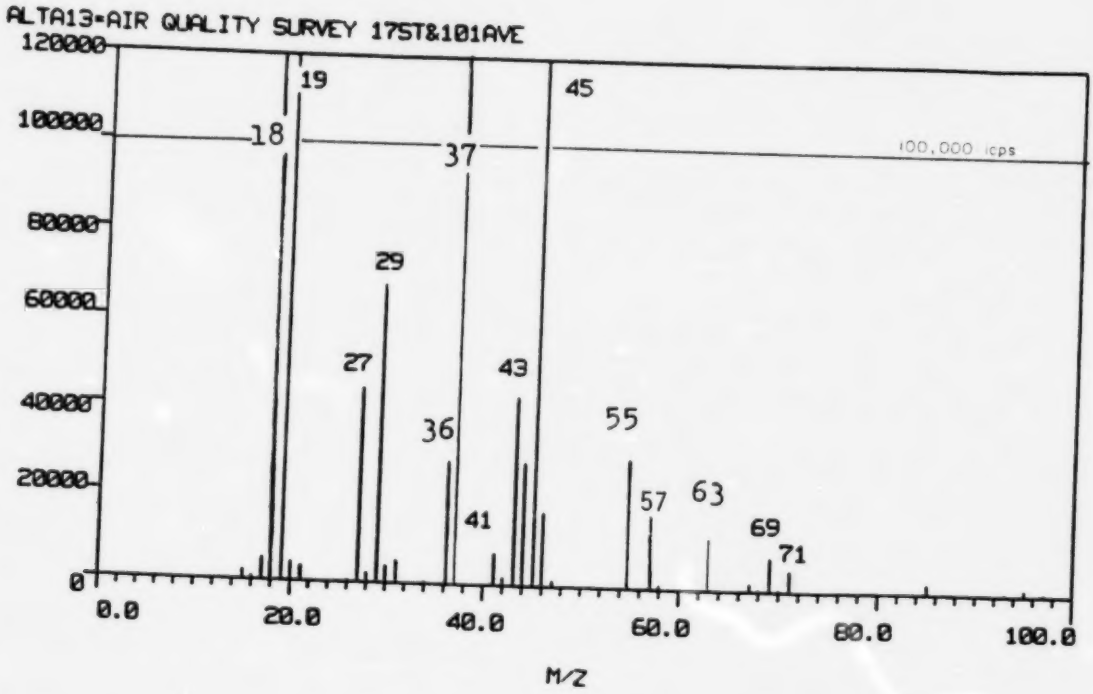
Assignments of mass-to-charge ratio (m/z) for peaks exceeding 10,000 counts/s but with less than 100,000 counts/s:

m/z	assignment	m/z	assignment
79	DMSO; benzene	112	fluoroaniline
80	pyridine	134	unidentified
93	glycerol; toluene	148	isatin; pthalimide
94	methylpyridine; aniline	162	aminoadipic acid
96	dimethylpyrrole; pyridine oxide	175	adipic acid dimethyl ester; dimethoxane
97	furfural	176	sulfanilyl fluoride
98	diallyamine	177	alkylated benzothiophene
100	cyclohexanone	222	bufencarb
110	aminophenol		

Figure 4 TAGA Mass Spectrum of Typical Downtown Air in a Canadian (Non-Alberta) City
(provided by Sciex, Inc.)

may be compared with Figure 5, extracted from the Sciex report for an east Edmonton/County of Strathcona location. The bottom half of Figures 2 and 3 list tentative compound identifications for only those peaks with greater than 100,000 ion counts/s. For Figures 4 and 5, identifications are provided for compounds one tenth as abundant (i.e. greater than 10,000 ion counts/s). In each case, this threshold eliminates the majority of peaks which are counted. The relationship between analytical sensitivity and the number of compounds identified is illustrated in Figure 6. Considering a threshold for including compounds at 100,000 ion counts/s, the spectra for room air with cigarette smoke has 13 peaks, breath of a cigarette smoker has 15 peaks, urban air from a Canadian city outside Alberta has 5 peaks and ambient air in east Edmonton/County of Strathcona has 4 peaks. As the threshold decreases, the number of compounds detected increases rapidly. Using a threshold of 10,000 counts/s, the corresponding spectra for the above samples have 104, 110, 23 and 13 peaks respectively. With a threshold of 1,000 counts/s, as used in the Sciex report, spectra for room air with cigarette smoke would have detected 176 species, breath from a cigarette smoker 194 species, downtown air in a Canadian city outside Alberta 207 species and an east Edmonton/County of Strathcona location 56 species.

Emission of a wide range of organic compounds from industrial and natural sources will cause organic compounds to be present at some level at almost any location. The number of



Assignments of mass-to-charge ratio (m/z) for peaks exceeding 100,000 counts/s:

m/z	assignment	m/z	assignment
18	ammonia	37	water
19	water	45	$C_2H_5O^+$ fragment

Assignments of mass-to-charge ratio (m/z) for peaks exceeding 10,000 counts/s but with less than 100,000 counts/s:

m/z	assignment	m/z	assignment
27	$C_2H_3^+$ fragment	46	dimethylamine; ethylamine
29	$C_2H_5^+$ fragment	55	water
36	ammonia	57	acrolein; $C_4H_9^+$ fragment
43	$C_2H_3O^+$fragment	63	ethylene glycol
44	ethylenimine		

Figure 5 TAGA Mass Spectrum of Air in East Edmonton/County of Strathcona from the Present Survey (Sciex Report)

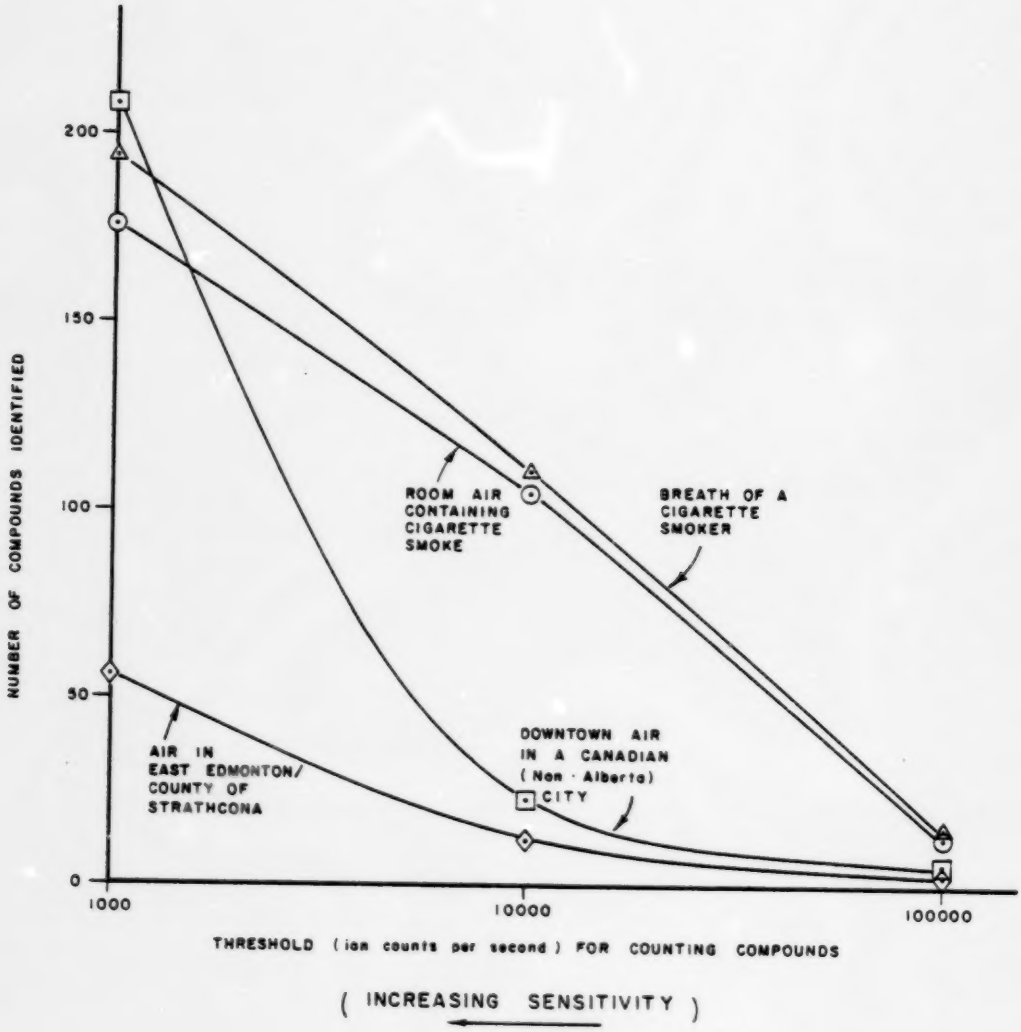


FIGURE 6. RELATIONSHIP BETWEEN ANALYTICAL SENSITIVITY AND THE NUMBER OF COMPOUNDS IDENTIFIED IN DIFFERENT SAMPLES.

compounds detected will depend on the analytical sensitivity of the instrument used. Extremely sensitive instruments will be capable of detecting many more compounds than less sensitive techniques. The instruments reviewed in this report must be considered extremely sensitive by current standards.

5. CONCLUSIONS

The two methods reviewed (if updated with more recent advances) represent the best available methods for identification and measurement of trace substances in the atmosphere. Both methods are capable of highly sensitive and accurate performance. They provide monitoring capabilities well beyond conventional air monitoring technology. These new technologies allow environmental studies to be designed to address the most complex and difficult air monitoring situations.

The reports documented the methods used and presented the data obtained without extensive interpretation. This was largely in accordance with the terms of reference for the studies. However, more information on criteria used for identification of compounds would have been useful for both reports.

The results by themselves do not provide a reliable basis to interpret air quality at any of the sites studied. In accordance with the demonstration nature of the studies, individual compound identifications were not verified, amounts of compounds were determined in only a few cases and sampling was not designed or evaluated to allow reliable characterizations of the atmosphere. Given these limitations, a conclusive interpretation of the data

with regard to environmental quality or public health is not possible. Some perspective was gained by comparing estimated concentrations of compounds with established occupational health criteria. These comparisons indicated that the levels reported outside of industrial property were well below those levels generally known to cause health effects. Hence, health effects would not be expected on the basis of the data reported by these two studies.

Overall the results must be considered together with the reality that the number of compounds detected is strongly influenced by the extreme sensitivity of the analytical techniques. As the sensitivity of air monitoring technology improves, the number of compounds detected by such methods must necessarily increase.

BIBLIOGRAPHY

SCIEX, "Air Quality Surveys in Alberta Using the TAGA 3000 Mobile Laboratory" Report to Alberta Environment, February 1982.

Strosher, M. T., "Trace Organic Compounds in the Atmosphere Near Industrial Development" Kananaskis Centre for Environmental Research. Report to Alberta Environment, February 1982.

APPENDIX 1 The Terms of Reference of the Contracts with Sciex, Inc. and Kananaskis Centre for Environmental Research

THE AGREEMENT BETWEEN ALBERTA ENVIRONMENT AND SCIEX, INC.

PROJECT OBJECTIVES

(i) To sample and analyze ambient air in the vicinity of selected industrial sites in the Province of Alberta using the TAGA^{TM} 3000 Mobile Laboratory.

(ii) To conduct pollutant composition analyses in the vicinity of the selected industrial sites.

(iii) To identify and track pollutants of concern in the vicinity of the selected industrial sites.

(iv) To conduct quantitative measurements of selected pollutants in the vicinity of the selected industrial sites.

THE AGREEMENT BETWEEN ALBERTA ENVIRONMENT AND SCIEX, INC.

TERMS OF REFERENCE

A. Work Program

The work program will include sampling and analyses in the vicinity of the following sources:

1. Oil sands plants north of Fort McMurray.
2. Waterton gas plant area south of Pincher Creek.
3. Compressor station sites - locations to be provided at later date.
4. Wood treating plant in Cochrane.
5. Industrial area of Fort Saskatchewan.
6. East Edmonton industrial area.

The Contractor will be advised of survey sampling sequence by the Minister, as the project progresses.

B. Timing and Duration

The work will be undertaken over the period of August 10, 1981 to December 15, 1981. Critical timing points will include:

(a) delivery of mobile vehicle containing the TAGA™ 3000 analyzer to Edmonton, Alberta, by August 28, 1981.

(b) submission of the final report to Alberta Environment within 60 days after completion of the survey program in Alberta.

The sources to be sampled may be altered at any time by the Minister.

The Contractor shall be prepared to conduct quantitative measurements of select compounds. Calibration standards for these select compounds will be provided by Alberta Environment.

THE AGREEMENT BETWEEN ALBERTA ENVIRONMENT AND SCIEX, INC.

The Contractor shall provide the necessary space, monitoring facilities, electrical power facilities and a sample splitter for 1-SO_2 analyzer, 1-NOx analyzer, 1-NO_2 analyzer, and 2-2-pen recorders inside the mobile laboratory. Alberta Environment will be responsible for mounting, operating, and dismantling of the SO_2, NOx and NO_2 analyzers.

The hours of operation for each day will be variable as the situation warrants and will be agreed upon by the Minister and the Contractor.

The Contractor shall provide to Alberta Environment within 60 days after completion of the survey program, all "raw" data obtained during the survey program.

The duration of the field work shall not exceed twelve instrument days of twelve hours per day.

THE AGREEMENT BETWEEN ALBERTA ENVIRONMENT AND THE KANANASKIS CENTER FOR ENVIRONMENTAL RESEARCH

Mass Spec. - G.C. Monitoring System Assessment

Term of Reference

(A) To carry out concurrent sampling in conjunction with the TAGA survey in the Pincher Creek - Waterton area, and in Cochrane or alternate site. Eight to twelve samples will be collected at each site. "Tenax" columns will be utilized for sampling and absorbed material will be analyzed using a fixed g.c. mass spec. unit.

(B)* To perform at least duplicate sampling at one of the sites to verify the data.

(C) To carry out concurrent sampling (2 to 4 samples) in the Fort Saskatchewan area or alternate site. The TAGA monitoring will be observed for assessment and evaluation of its operation while at this site.

(D) To provide a report of the findings approximately three months after completion of sampling, analyses and observations. Report will include the qualitative and quantitative data acquired at the sampled sites (in comparison with TAGA results) and to include general comments as far as the comparison.

* Alberta Environment has agreed to forgo duplicate sampling in order to do more sampling at different sites.

APPENDIX 2 Data on Tenax and Chromosorb 101

TENAX-GC AS A TRAPPING MATERIAL*

Tenax-GC was originally created to serve as a GC column packing. But it has also been shown to be an excellent material for adsorbing volatiles from air for subsequent analysis. Because of its good thermal stability, Tenax-GC can be employed for the collection and desorption of volatile substances with molecular weights ranging up to several hundred, making it ideal for trace analysis of biologically important volatiles and air pollutants.

The advantages of Tenax-GC over other materials tried for trapping are efficient adsorption of volatiles at room temperature and efficient desorption of the same materials at 300°C, a temperature that Tenax-GC easily withstands. Less than 4 hours are required for trapping and analysis of complex samples. The stability of volatile organics trapped on the Tenax-GC appears to be excellent and trapped samples can easily be stored or shipped to another laboratory for analysis. Reproducibility appears excellent. It was found that the volatiles from a single urine sample can be collected in multiple parallel Tenax-GC traps and reproducible GC results obtained[4]. This allows GC analysis of volatiles from the same urine sample with a flame ionization detector, a flame photometric detector, and GC/MS. Volatiles collected in the Tenax-GC traps can be stored for at least two weeks[4]. Traps stored at 0°C, 4°C, and room temperature give reproducible GC results[3].

Applications

As reported by Bertsch, Zlatkis, Liebich, and Schneider at the Ninth International Symposium on Advances in Chromatography[1], Tenax-GC was used to concentrate volatiles in the atmosphere of Skylab 4. The requirements that the sampling system had to satisfy include: 1) Efficient concentration of volatiles from a large air sample with no interference from moisture, 2) Complete collection in the volatile range considered and quantitative regeneration, 3) Storage capability for later analysis or potential for a simple automated procedure on board, 4) Short sampling interval to follow rapid compositional changes.

Tenax-GC was completely effective in fulfilling all the above requirements. With the aid of Tenax-GC, about 140 volatile substances were detected in Skylab's atmosphere at levels greater than 0.007%. Major components proved to be Freon 113 and acetone, which together made up about 49% of the sample.

Tenax-GC is also effective for trapping volatile organic constituents of urine, human breath, and environmental air for subsequent GC analysis. Dr. A. Zlatkis and coworkers described the method in the February 1973 issue of *Chromatographia*, where the apparatus and preliminary results are presented. They subsequently reported on the use of this technique for the study of volatile metabolites of urine samples from normal individuals and samples from individuals with diabetes.

Trapping Apparatus

The trapping apparatus and procedures are relatively simple. The trap is a glass tube, 11 cm x 8 mm ID x 10 mm OD, partially packed with 2 ml of Tenax-GC. The Tenax-GC trap is first preconditioned with helium flow at 375°C for 30 minutes and then connected to the end of a water condenser with a Teflon sleeve. Volatiles from urine heated at 100°C are swept through the condenser into the trap by means of helium flow through the system. Air and breath samples are pulled through the condenser into the trap by vacuum. The trap is maintained at room temperature.

The trap is then inserted into a modified GC injection port which is connected to a precolumn cooled by dry ice in the GC oven. The trapped volatiles are desorbed from the trap at 300°C with helium flow and collected in the precolumn. The precolumn is then connected to the GC column, the dry ice removed, and the analysis started at room temperature. The precolumn and the GC column contain the same liquid phase.

For the work reported[2,3,4], 3 meter or 10 ft x 1 mm ID capillary precolumns and 100 meter or 300 ft x 0.5 mm ID nickel capillary GC columns, all coated with Emulphor ON-870 liquid phase, were used. The analyses were run at room temperature for 15 minutes, then 80°C for 15 minutes, and then temperature programmed up to 175°C or 190°C at 2°C/min (0.5°C/min for air samples).

We urge anyone interested in or in need of an efficient process for collecting volatile samples to read these papers by Dr. Zlatkis and his co-workers.

References

1. Bertsch, W., A. Zlatkis, H.M. Liebich, and H.J. Schneider, J. Chromatogr., 99: 673 (1974).
2. Zlatkis, A., H.A. Lichtenstein, and A. Tishbee, Chromatographia, 6: 67 (1973).
3. Zlatkis, A., W. Bertsch, H.A. Lichtenstein, A. Tishbee, F. Shumbo, H.M. Liebich, A.M. Coscia, and N. Fleischer, Anal. Chem., 45: 763 (1973).
4. Zlatkis, A., H.A. Lichtenstein, A. Tishbee, W. Bertsch, F. Shumbo, and H.M. Liebich, J. Chromatogr. Sci., 11: 299 (1973).
5. *Novotny, M., M.L. Lee, and K.D. Bartle, Chromatographia, 7: 333 (1974).
6. *Bellar, T.A., and J.J. Lichtenberg, J. Am. Water Works Assoc., 66: 739 (1974).
7. *Politzer, I.R., S. Githens, B.J. Dowty, and J.L. Laseter, J. Chromatogr. Sci., 13: 378 (1975).
8. *Butler, L.D., and M.F. Burke, J. Chromatogr. Sci., 14: 117 (1976).

*Additional applications not discussed in this article.

*The 20/35 mesh size of Tenax-GC is designed specifically for adsorption of volatile organics.

CHROMOSORB CENTURY SERIES 101-108
POROUS POLYMERS

Chromosorb porous polymers are designed to perform a wide variety of chromatographic separations. Some suggested uses for the various types are given below. 101 — Fast, efficient separation of free fatty acids, glycols, alkanols, alkanes, esters, ketones, aldehydes and ethers. 102 — High surface area polymer causing no tailing of water, alcohols, or most other oxygenated compounds. Useful for light and permanent gases and low molecular weight compounds. 103 — Fast, efficient separation of amines, amides, alcohols, aldehydes, hydrazines and ketones. 104 — For nitriles, nitro-paraffins, aqueous hydrogen sulfide, xylenols, oxides of nitrogen and ammonia. Different retention characteristics and selectivity than above grades. 105 — Provides efficient separation of aqueous mixtures containing formaldehyde, acetylene from lower hydrocarbons, and most gases and organic compounds in the boiling range up to 200°C. 106 — Highly efficient in resolving lower fatty acids from fatty alcohols. 107 — Separates various classes of compounds, and formalin in particular. 108 — Provides outstanding separations of gases and polar materials such as water, alcohols, aldehydes, ketones, glycols, etc.

TABLE I. TYPICAL PHYSICAL PROPERTIES OF THE VARIOUS CHROMOSORB POLYMERS

Physical Properties	101	102	103	104	105	106	107	108
Type	STY-DVB	STY-DVB	Cross-linked Polystyrene	ACN-DVB	Polyaromatic	Cross-linked Polystyrene	Cross-linked Acrylic Ester	Cross-linked Acrylic Ester
Free Fall Density (g/cc)	0.30	0.29	0.32	0.32	0.34	0.28	0.30	0.30
Surface Area (m_2/g)	Less than 50	300-400	15-25	100-200	600-700	700-800	400-500	100-200
Average Pore Diameter (μ)	0.3-0.4	0.0085	0.3-0.4	0.06-0.08	0.04-0.06	50 A	90 A	235 A
Water Affinity	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic
Color	White	White	White	White*	White	White	White	White
Temp. Limit (isothermal) °C	275	250	275	250	250	250	250	250
Temp. Limit (programmed) °C	325	300	300	275	275	275	275	275

*Turns yellow after column conditioning and brown after extended use. This in no way affects column performance.